

# Synthesis, Crystal Structure and Fluorescent Properties of Silver and Cadmium Complexes

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**ABSTRACT** Two new complexes  $[\text{Ag}(\text{bix})]_n \cdot n\text{NAA} \cdot n\text{H}_2\text{O}$  (**1**) and  $[\text{Cd}(\text{NAA})(\text{phen})_2(\text{H}_2\text{O})]_2 \cdot 2\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$  (**2**) (bix = 1,4-bis(imidazol-1-ylmethyl)benzene, HNAA =  $\alpha$ -naphthylacetic acid, phen = 1,10-phenanthroline) have been successfully synthesized under hydrothermal conditions. Their structures have been determined by elemental analyses, IR spectroscopy, TG and single-crystal X-ray diffraction analysis. The intermolecular hydrogen bonding or  $\pi$ - $\pi$  stacking interactions extend the complexes into a 3D supramolecular structure. Moreover, the luminescent properties of complex **2** have been investigated in the solid state.

**Keywords:** hydrothermal synthesis; crystal structure; Ag(I) complex; Cd(II) complex;

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## 1 INTRODUCTION

Metallosupramolecular species assembled from transition metals and organic bridging ligands with novel structures and properties have been rapidly developed because of their intriguing structural diversity and potential applications as functional materials<sup>[1-5]</sup>. However, the rational design of new materials for special applications is still at an early evolutionary stage with the current focus mainly on understanding the factors to determine the crystal packing. During the last few years, several types of forces, such as coordination bonding<sup>[6-8]</sup>, hydrogen bonding<sup>[9-11]</sup>,  $\pi$ - $\pi$  stacking<sup>[12, 13]</sup> and electrostatic interactions<sup>[14]</sup>, have been well used in constructing extended supramolecular networks. Up to now, the most important driving forces in crystal engineering are coordination, hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions, and many networks assembled from mono- or polynuclear metal complexes via hydrogen bonding and  $\pi$ - $\pi$  stacking interactions have been reported recently<sup>[15]</sup>. The unique strength, directionality and complementary of such non-covalent interactions play key roles in the construction of various architectures for molecular self-assembly and recognition<sup>[16, 17]</sup>.

Considering all the aspects stated above, here we report the syntheses and crystal structures of two

coordination supramolecules,  $[\text{Ag}(\text{bix})]_n \text{nNAA} \cdot \text{nH}_2\text{O}$  (**1**) and  $[\text{Cd}(\text{NAA})(\text{phen})_2(\text{H}_2\text{O})]_2 \cdot 2\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$  (**2**). In the solid state, complexes **1** and **2** both form three-dimensional (3D) networks resulted from intermolecular hydrogen-bonding or  $\pi$ - $\pi$  stacking interactions.

## 2 EXPERIMENTAL

### 2.1 Materials and instruments

All the chemicals for synthesis were commercially purchased and used without further purification. Elemental analyses of C, H and N were performed on an Elementar Vario III Elemental Analyzer. IR spectrum was recorded in the range of  $4000\sim 400\text{ cm}^{-1}$  on a Nicolet 6700 spectrometer using a KBr pellet. Thermal stability (TG-DTA) studies were carried out on a Dupont thermal analyzer from room temperature to  $800\text{ }^\circ\text{C}$ . Powder X-ray diffraction (PXRD) patterns were collected in the  $2\theta$  range of  $5\sim 50^\circ$  with a scan speed of  $0.1\text{ }^\circ\text{S}^{-1}$  on a Bruker D8 Advance instrument using a  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056\text{ \AA}$ ) at room temperature. The fluorescent studies were carried out on a computer-controlled JY Fluoro-Max-3 spectrometer at room temperature.

### 2.2 Synthesis

$[\text{Ag}(\text{bix})]_n \text{nNAA} \cdot \text{nH}_2\text{O}$  (**1**) Complex **1** was prepared by the reaction of  $\text{Ag}(\text{OAc})$  with  $\alpha$ -naphthylacetic acid and 1,4-bis(imidazol-1-ylmethyl)benzene in an equimolar ratio in the mixed solvents of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ . Suitable amount of  $\text{NaOH}$  was added to this solution to adjust the pH value to 7 and it was stirred at room temperature for 0.5 h until a homogeneous solution was obtained. Then it was sealed in an acid digestion bomb (30 mL) at  $140\text{ }^\circ\text{C}$  for 5 days. After the reaction system was slowly cooled to room temperature, colorless block crystals were obtained by filtration and dried in air. The yield of the target complex is ca. 21% (based on Ag salt). Anal. Calcd. for  $\text{C}_{26}\text{H}_{23}\text{AgN}_4\text{O}_3$ : C, 57.05; H, 4.24; N, 10.24%. Found: C, 56.93; H, 4.05; N, 9.97%. IR (KBr pellet,  $\text{cm}^{-1}$ ) spectra: 3385w, 3103w, 1565s, 1512w, 1379s, 1230w, 1074w, 792w, 710w, 650w, 539w.

$[\text{Cd}(\text{NAA})(\text{phen})_2(\text{H}_2\text{O})]_2 \cdot 2\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$  (**2**) Complex **2** was prepared from a mixture of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.026 g, 0.1 mmol), HNNA (0.019 g, 0.1 mmol), phen (0.04 g, 0.2 mmol) and  $\text{H}_2\text{O}$  (18 mL) in a 30 mL Teflon-lined stainless steel vessel, and then the vessel was sealed and heated at  $130\text{ }^\circ\text{C}$  for 5 days. After the reaction mixture was slowly cooled down to room temperature at the rate of  $5\text{ }^\circ\text{C/h}$ , colorless block crystals of complex **2** were obtained. Yield: 27% (based on Cd salt). Anal. Calcd. (%) for  $\text{C}_{76}\text{H}_{52}\text{Cd}_2\text{N}_8\text{O}_{11}$ : C, 61.76; H, 3.55; N, 7.58. Found (%): C, 61.08; H, 3.07; N, 7.01. IR ( $\text{cm}^{-1}$ ): 3058w, 1584s, 1570w, 1378s, 1324w, 1144w,

848w, 722m, 632w.

### 2.3 X-ray crystallography

All diffraction data of complexes **1** and **2** were collected on a Bruker/Siemens Smart Apex II CCD diffractometer with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K. Data reductions and absorption corrections were performed using the SAINT and SADABS programs, respectively. The structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on  $F^2$  by full-matrix least-squares techniques using the SHELXL-97 crystallographic software package<sup>[18]</sup>. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. For **1**, a total of 4557 reflections were collected in the range of  $2.03 \leq \theta \leq 26.03^\circ$ , of which 3601 were independent ( $R_{\text{int}} = 0.0194$ ). The final  $R = 0.0455$  and  $wR = 0.1137$  for observed reflections with  $I > 2\sigma(I)$ , and  $R = 0.0587$  and  $wR = 0.1217$  for all data with  $(\Delta\rho)_{\text{max}} = 0.900$  and  $(\Delta\rho)_{\text{min}} = -0.802$  e Å<sup>-3</sup>. For **2**, a total of 12668 reflections were collected in the range of  $1.07 \leq \theta \leq 26.15^\circ$ , of which 7090 were independent ( $R_{\text{int}} = 0.0710$ ). The final  $R = 0.0551$  and  $wR = 0.1112$  for observed reflections with  $I > 2\sigma(I)$ , and  $R = 0.0950$  and  $wR = 0.1220$  for all data with  $(\Delta\rho)_{\text{max}} = 0.789$  and  $(\Delta\rho)_{\text{min}} = -0.396$  e Å<sup>-3</sup>. Selected bond lengths and bond angles of complexes **1** and **2** are shown in Table 1.

## 3 RESULTS AND DISCUSSION

### 3.1 Structural description

Single-crystal X-ray diffraction analysis indicates that complex **1** crystallizes in  $P2_1/n$  space group and comprises of a one-dimensional chain-like structure. There are one Ag(I) ion, one bix ligand, one HNAA ligand and one crystal water molecule in the asymmetric unit (Fig. 1). Please note, the HNAA ligand does not coordinate with the Ag(I) ion, and it's just a balanced charge. The Ag(1) ion is coordinated by two nitrogen atoms from two bix ligands (Ag(1)–N(1) = 2.127(3), Ag(1)–N(4A) = 2.136(3) Å). The coordination angle round the Ag ion is 168.51(12)°.

In the crystal structure of complex **1**, the bix ligands adopt a *trans*-conformation bridging mode with a dihedral angle between two imidazole rings of 24.07° and link the Ag(I) ions to form a one-dimensional zigzag chain-like structure with the Ag...Ag distance of 14.301 Å. The Ag(1) ion shows a slightly distorted linear coordination construction. It is worthwhile to note that free  $\alpha$ -naphthylacetic acid and neighboring bix ligand contribute to the formation of the chain by C–H...O and O–H...O hydrogen bonding interactions (Table 2). In

addition, the one-dimensional trapezoidal banded structure is formed between the adjacent one-dimensional chains and  $\alpha$ -naphthylacetic acid through C–H $\cdots$ O and O–H $\cdots$ O hydrogen bonding interactions. It is noteworthy that there exist important C–H $\cdots\pi$  interactions between C(4) and benzene ring C(5)~C(9) (symmetry code:  $1-x, 1-y, -z$ ), C(11) and benzene ring C(17)~C(22) (symmetry code:  $1/2+x, 1/2-y, -1/2+z$ ), C(13) and benzene ring C(21)~C(26) (symmetry code:  $1/2+x, 1/2-y, -1/2+z$ ), C(24) and benzene ring C(5)~C(9) (symmetry code:  $1/2+x, 1/2-y, 1/2+z$ ), from symmetry-related bix and NAA ligands with the C–H $\cdots\pi$  distances of 3.377(4), 3.829(5), 3.825(5), 3.580(10) Å, respectively. In this mode, the two-dimensional layered structure comes into being (Fig. 2).

A single-crystal X-ray diffraction study reveals that complex **2** crystallizes in monoclinic  $P2_1/n$  space group. The coordination environment of Cd(II) in **2** is shown in Fig. 3. There are two coordination centers, Cd(1) and Cd(2), in the crystal with the same coordination modes, four phen ligands, two HNAA ligands, two coordinated water molecules, one crystal water molecule and two free acetates. The Cd(1) ion is six-coordinated by four nitrogen atoms from two different phen ligands (Cd(1)–N(1) = 2.429(4), Cd(1)–N(2) = 2.371(4), Cd(1)–N(3) = 2.381(4), Cd(1)–N(4) = 2.385(4) Å), one carboxylate oxygen atom (Cd(1)–O(1) = 2.183(4) Å) from the HNAA ligand and one coordinated water molecule (Cd(1)–O(2W) = 2.291(3) Å) to furnish a distorted octahedral coordination architecture. The coordination angles around the Cd atom are in the range of 69.07(15)~161.00(15)°. In the coordination environment, one carboxylate oxygen atom (O(1)) and three nitrogen atoms (N(2), N(3) and N(4)) are located in the basal plane, whereas the other nitrogen atom (N(1)) and coordinated water molecule (O(2W)) occupy the axial positions from the opposite directions. It is noteworthy that the acetate does not coordinate with Cd(I) ion, and it's just a balanced charge.

In the crystal structure of complex **2**, phen ligands adopt a classic bidentate chelating mode, and HNAA ligand displays one kind of coordination modes, namely a monodentate bridging mode. In the structure unit, the up and down independent structure is connected to a stable structure through O–H $\cdots$ O, C–H $\cdots$ O hydrogen bonding (Table 2) and  $\pi$ - $\pi$  stacking (Table 3) between pyridine ring of phen ligands and benzene ring of phen and NAA ligands. Moreover, each structure unit is linked into a double-chain by O–H $\cdots$ O and C–H $\cdots$ O hydrogen bonding interactions. Moreover, the two-dimensional layer architecture is formed between the double-chain by means of O–H $\cdots$ O, C–H $\cdots$ O hydrogen bonding and  $\pi$ - $\pi$  stacking interactions, which are connected with free acetate to form a three-dimensional supramolecular structure by O–H $\cdots$ O, C–H $\cdots$ O hydrogen bonding (Fig. 4).

### 3.2 IR analysis of complex 1

IR spectrum of **1** shows a broad absorption band at  $3385\text{ cm}^{-1}$  corresponding to the  $\text{H}\cdots\text{O}$  stretching of crystal water molecules in the complex. Asymmetric and symmetric  $\text{COO}^-$  stretching modes of the lattice  $\text{NAA}^-$  anion were evidenced by very strong, slightly broadened bands at  $1565$  and  $1379\text{ cm}^{-1}$ <sup>[19]</sup>, which is consistent with the results of X-ray analysis.

IR spectrum of **2** shows a broad absorption band at  $3058\text{ cm}^{-1}$  corresponding to the  $\text{H}\cdots\text{O}$  stretching of water molecule in the complex. Asymmetric and symmetric  $\text{COO}^-$  stretching modes of the lattice  $\text{NAA}^-$  anion were evidenced by very strong, slightly broadened bands at  $1584$  and  $1378\text{ cm}^{-1}$ <sup>[19]</sup>, which is consistent with the results of X-ray analysis.

### 3.3 Thermal stability and powder X-ray diffraction (PXRD)

To confirm the phase purity of complexes **1** and **2**, powder X-ray diffraction (PXRD) patterns were recorded for **1** and **2**, and it was comparable to the corresponding simulated patterns calculated from the single-crystal diffraction data (Fig. 5), indicating a pure phase of bulky sample.

In order to better understand the thermal stability of complexes **1** and **2**, its thermal decomposition behaviors were investigated at  $50\sim 800\text{ }^\circ\text{C}$  under nitrogen atmosphere (Fig. 6). The TG curve of **1** indicates a weight loss of 3.10% from  $50$  to  $70\text{ }^\circ\text{C}$  corresponding to the departure of crystal water molecule (calcd. 3.28%). The TG curve presents a platform and the framework starts to decompose at  $170\text{ }^\circ\text{C}$ . The TG curve of **2** represents a weight loss of 10.00% from  $50$  to  $252\text{ }^\circ\text{C}$  due to the departure of water molecule and acetate (calcd. 10.65%). The TG curve presents a platform and the framework starts to decompose at  $255\text{ }^\circ\text{C}$ .

### 3.4 Photoluminescent properties

The emission spectrum of complex **2** in the solid state at room temperature is exhibited in Fig. 7. It can be observed that **2** exhibits blue photoluminescence with an emission maximum at *ca.*  $465\text{ nm}$  upon excitation at  $325\text{ nm}$ . In order to realize the nature of these emission bands, we first studied the photoluminescence properties of free HNAA ( $\lambda_{\text{em}} = 275\text{ nm}$ ) ligand, and proved that it does not emit any luminescence in the range of  $400\sim 800\text{ nm}$ . And then we researched the emission spectrum of phen ( $\lambda_{\text{em}} = 285\text{ nm}$ ) itself and the result revealed that it does not emit any luminescence in the range of  $400\sim 800\text{ nm}$ , which has also been proved previously. Thus, on the basis of the earlier literature<sup>[20]</sup>, the emission band could be assigned to the emission of ligand-to-metal charge transfer (LMCT).

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**Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1 and 2**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Ag(1)–N(1)	2.127(3)	Ag(1)–N(4A)	2.136(3)		

Angle (°)	Angle (°)	Angle (°)
N(1)–Ag(1)–N(4A) 168.51(12)		
<b>2</b>		
Bond Dist.	Bond Dist.	Bond Dist.
Cd(1)–O(1) 2.183(4)	Cd(1)–O(2W) 2.291(3)	Cd(1)–N(1) 2.429(4)
Cd(1)–N(2) 2.371(4)	Cd(1)–N(3) 2.381(4)	Cd(1)–N(4) 2.385(4)
Cd(2)–O(3) 2.190(4)	Cd(2)–O(1W) 2.307(3)	Cd(2)–N(5) 2.372(4)
Cd(2)–N(6) 2.392(4)	Cd(2)–N(7) 2.416(4)	Cd(2)–N(8) 2.383(4)
Angle (°)	Angle (°)	Angle (°)
O(1)–Cd(1)–O(2W) 108.64(15)	O(1)–Cd(1)–N(2) 102.61(16)	O(2W)–Cd(1)–N(2) 89.16(14)
O(1)–Cd(1)–N(3) 158.88(16)	O(2W)–Cd(1)–N(3) 86.66(13)	N(2)–Cd(1)–N(3) 91.80(14)
O(1)–Cd(1)–N(4) 91.30(16)	O(2W)–Cd(1)–N(4) 107.40(14)	N(2)–Cd(1)–N(4) 153.87(14)
N(3)–Cd(1)–N(4) 69.79(15)	O(1)–Cd(1)–N(1) 85.69(15)	O(2W)–Cd(1)–N(1) 156.42(14)
N(2)–Cd(1)–N(1) 69.07(15)	N(3)–Cd(1)–N(1) 85.16(13)	N(4)–Cd(1)–N(1) 90.39(14)
O(3)–Cd(2)–O(1W) 106.69(14)	O(3)–Cd(2)–N(5) 93.10(15)	O(1W)–Cd(2)–N(5) 108.01(13)
O(3)–Cd(2)–N(8) 100.29(15)	O(1W)–Cd(2)–N(8) 87.29(13)	N(5)–Cd(2)–N(8) 155.94(14)
O(3)–Cd(2)–N(6) 161.00(15)	O(1W)–Cd(2)–N(6) 87.12(13)	N(5)–Cd(2)–N(6) 69.82(15)
N(8)–Cd(2)–N(6) 93.21(14)	O(3)–Cd(2)–N(7) 83.50(14)	O(1W)–Cd(2)–N(7) 155.95(13)
N(5)–Cd(2)–N(7) 92.77(14)	N(8)–Cd(2)–N(7) 69.25(14)	N(6)–Cd(2)–N(7) 88.92(14)

Symmetry transformations used to generate the equivalent atoms: 1: A:  $x-1, y, z+1$

**Table 2. Hydrogen Bonds for Complexes 1 and 2**

D–H ...A	d(D–H)	d(H ...A)	d(D ...A)	∠(DHA)	Symmetry codes
<b>1</b>					
O(1W)–H(1WA) ...O(1)	1.07	1.84	2.881(5)	164	1+x, y, z
O(1W)–H(1WB) ...O(2)	0.95	1.77	2.722(4)	175	1–x, –y, –z
C(2)–H(2) ...O(1)	0.93	2.54	3.197(5)	128	–1/2+x, 1/2–y, 1/2+z
C(8)–H(8) ...O(1)	0.93	2.57	3.387(5)	147	1/2+x, 1/2–y, 1/2+z
C(12)–H(12) ...O(2)	0.93	2.30	3.140(5)	149	1/2+x, 1/2–y, –1/2+z
<b>2</b>					
O(3W)–H(3WA) ...O(6)	0.85	2.42	2.988 (8)	125	1–x, –y, 1–z
O(3W)–H(3WB) ...O(6)	0.85	2.49	3.303(8)	160	–1/2+x, 1/2–y, 1/2+z
C(5)–H(5) ...O(8)	0.93	2.59	3.471(7)	158	1/2+x, 1/2–y, 1/2+z
C(15)–H(15) ...O(6)	0.93	2.28	3.205(9)	176	1–x, 1–y, 1–z
C(20)–H(20) ...O(7)	0.93	2.53	3.240(9)	133	1/2–x, 1/2+y, 1/2–z
C(26)–H(26A) ...O(7)	0.97	2.57	3.541(8)	176	1/2–x, –1/2+y, 1/2–z
C(44)–H(44) ...O(8)	0.93	2.56	3.350(8)	143	1/2–x, –1/2+y, 1/2–z
C(50)–H(50) ...O(8)	0.93	2.52	3.377(8)	154	1/2–x, 1/2+y, 1/2–z
C(65)–H(65) ...O(5)	0.93	2.58	3.192(12)	124	1–x, –y, –z

**Table 3. Parameters between the Planes in 2**

Plane	Distance between ring	Dihedral Angle (°)	Perpendicular distance	Perpendicular distance Of plane (J) on ring I
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	Centroids (Å)		of plane (I) on ring J (Å)	
N(2)C(10)C(9)C(8)C(7)C(11)→C(31)C(32)C(33)C(34)C(35)C(36) <sup>i</sup>	3.652(5)	2.5(4)	3.567(2)	−3.570(4)
N(4)C(22)C(21)C(20)C(19)C(23)→N(5)C(37)C(38)C(39)C(40)C(48)	3.799(3)	1.0(2)	3.476(2)	3.492(2)
N(4)C(22)C(21)C(20)C(19)C(23)→C(40)C(41)C(42)C(43)C(47)C(48)	3.610(3)	2.1(2)	−3.471(2)	3.446(2)
C(4)C(5)C(6)C(7)C(11)C(12)→C(27)C(28)C(29)C(30)C(31)C(36) <sup>i</sup>	3.999(5)	4.1(3)	3.497(2)	−3.584(3)
C(4)C(5)C(6)C(7)C(11)C(12)→C(31)C(32)C(33)C(34)C(35)C(36) <sup>i</sup>	3.953(5)	3.4(4)	3.514(2)	−3.582(4)
C(16)C(17)C(18)C(19)C(23)C(24)→N(5)C(37)C(38)C(39)C(40)C(48)	3.636(3)	1.5(2)	−3.450(2)	3.476(2)
N(8)C(49)C(50)C(51)C(52)C(60)→C(67)C(68)C(69)C(70)C(71)C(72) <sup>ii</sup>	3.913(4)	5.7(3)	−3.685(2)	3.585(3)
C(52)C(53)C(54)C(55)C(59)C(60)→C(67)C(68)C(69)C(70)C(71)C(72) <sup>ii</sup>	3.806(5)	4.9(3)	−3.472(2)	3.590(3)

Symmetry codes: i =  $-x, -1-y, -z$ ; ii =  $1-x, 1-y, -z$

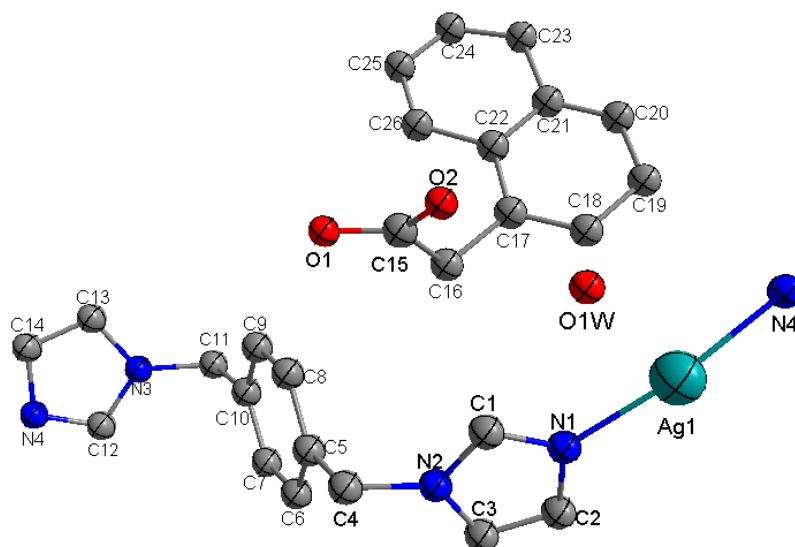


Fig. 1. View of the asymmetric unit of complex 1. All hydrogen atoms are omitted for clarity

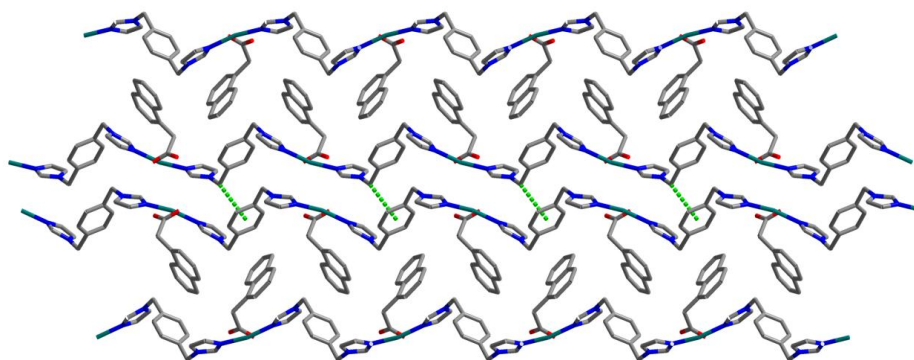


Fig. 2. View of the two-dimensional layered structure by C–H... $\pi$  interactions in complex 1



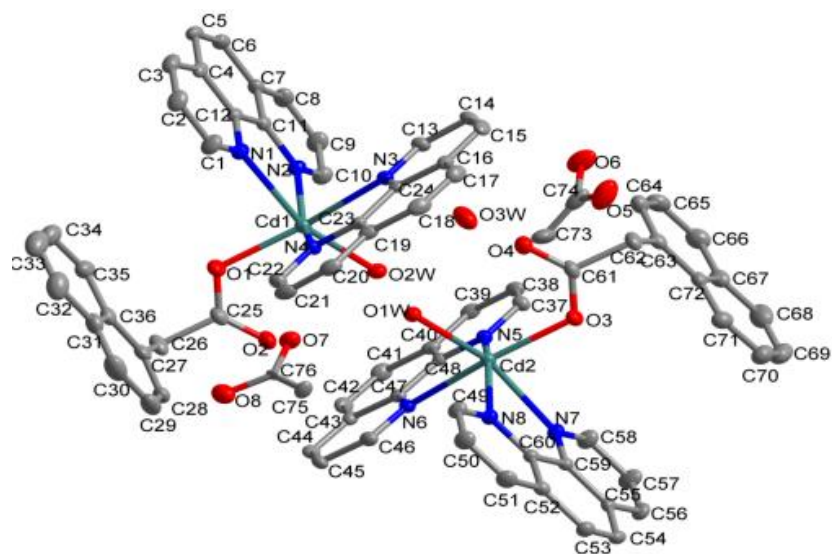


Fig. 3. View of the asymmetric unit of complex 2. All hydrogen atoms are omitted for clarity

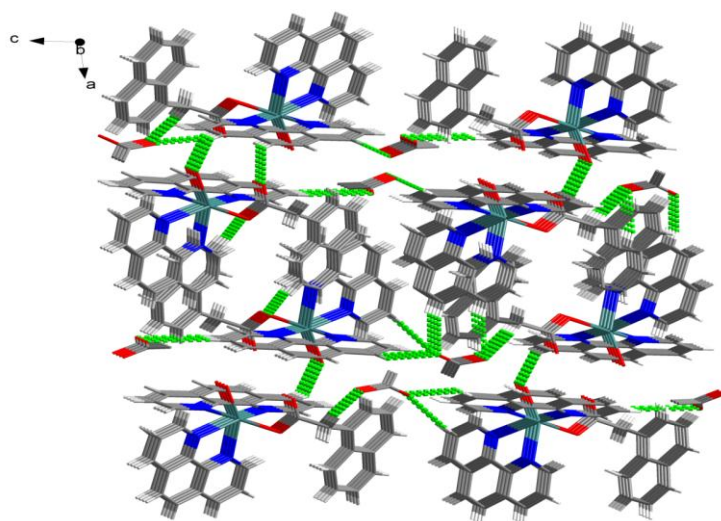


Fig. 4. View of the 3D supramolecular structure of 2

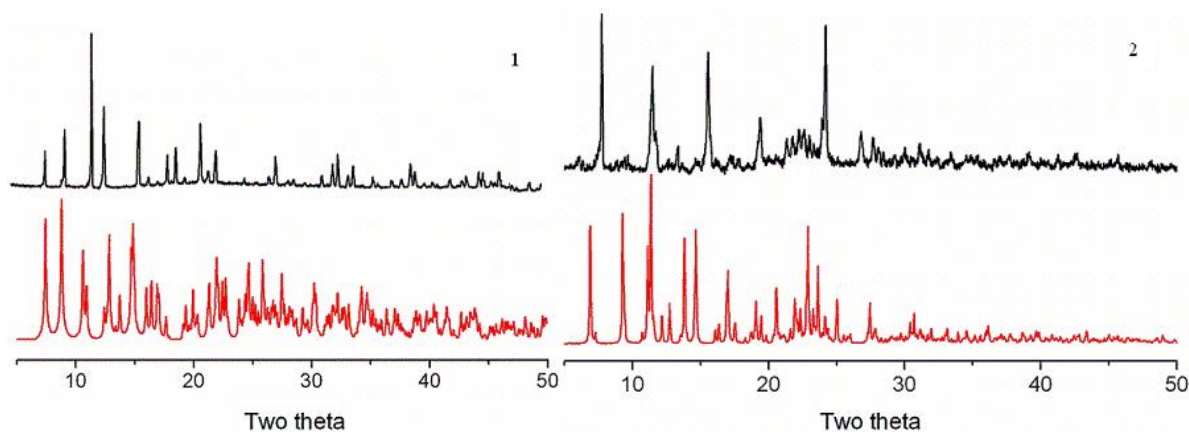


Fig. 5. PXRD analysis of the title complex 1: bottom-simulated, top-experimental

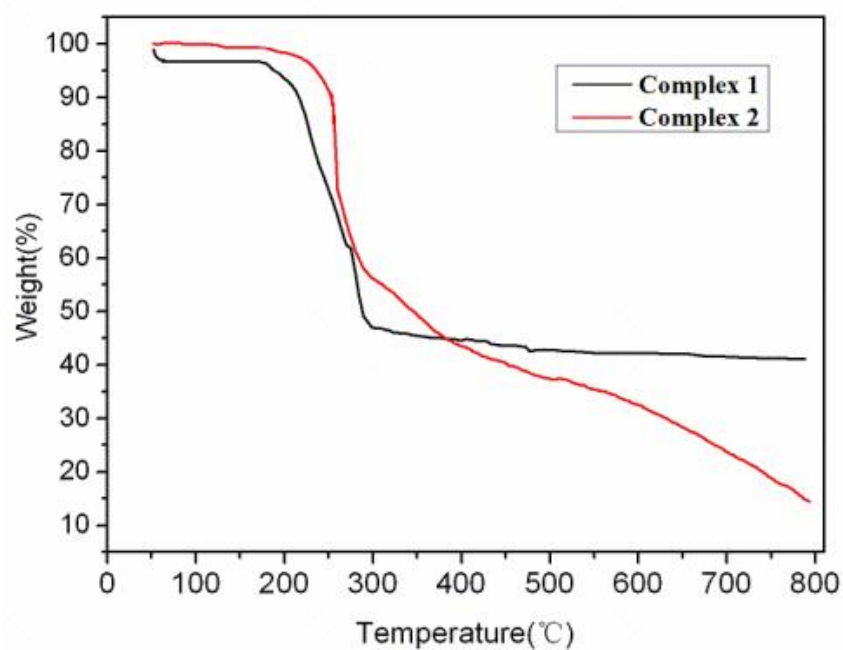


Fig. 6. TG curves of complexes 1 and 2

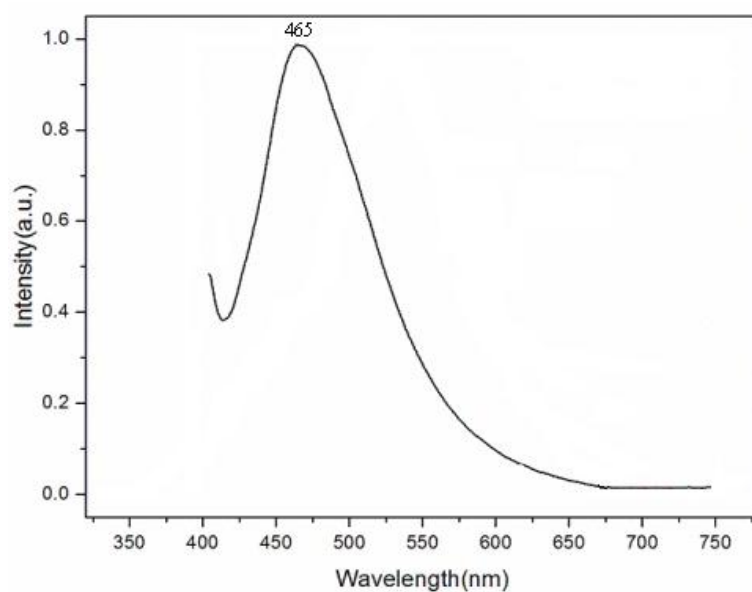


Fig. 7. Solid-state emission spectrum of 2 at room temperature

## Synthesis, Crystal Structure and Fluorescent Properties of Silver and Cadmium Complexes

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Two new complexes  $[\text{Ag}(\text{bix})]_n \cdot n\text{NAA} \cdot n\text{H}_2\text{O}$  (**1**) and  $[\text{Cd}(\text{NAA})(\text{phen})_2(\text{H}_2\text{O})]_2 \cdot 2\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$  (**2**) (bix = 1,4-bis(imidazol-1-ylmethyl)benzene, HNAA =  $\alpha$ -naphthylacetic acid, phen = 1,10-phenanthroline) have been successfully synthesized under hydrothermal conditions. Their structures have been determined by elemental analyses, IR spectroscopy, TG and single-crystal X-ray diffraction analysis. The intermolecular hydrogen bonding or  $\pi$ - $\pi$  stacking interactions extend the complexes into a 3D supramolecular structure. Moreover, the luminescent properties of complex **2** have been investigated in the solid state.

